Polyelectrolytes in Solution- Recent Computer Simulations

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Abstract

We present a short overview over recent MD simulations of systems of fully flexible polyelectrolyte chains with explicitly treated counter ions using the full Coulomb potential. The main emphasis is given on the conformational properties of the polymers, with a short discussion on counter ion condensation.

1 INTRODUCTION

Polyelectrolytes represent a broad and very interesting class of materials [1] that enjoys an increasing attention in the scientific community. Even though the theory of neutral polymer systems is well developed, polyelectrolytes remain one of the least understood states of the soft matter area. Theoretically this is mainly due to the long range Coulomb interaction. Simple scaling theories, which have been proven so successfully in neutral polymer theory, have to deal with the additional length scales set by the electrostatic interaction. It is the delicate interplay between electrostatic interaction, and the conformational degrees of freedom, which in turn are governed by a host of short range interactions, which proves to be a difficult question for the theory. This results in essence in the fact that the analytical theory is only able to treat two limiting cases, namely the case of high salt excess, resulting in effectively screening down the electrostatic interaction to treat it as a perturbation, or the case of an overwhelming dominance of the Coulomb force, which results in a strongly elongated chain. Unfortunately it is just the intermediate case, which proves to be the most interesting regime in terms of application, experiment and theory.

How difficult it is for the analytical theory to treat this intermediate regime could be seen in the recent controversy over the correct exponent y, which governs the variation of the electrostatic persistence length L_e with Debye screening length r_D. The theory is already simplified because instead of the full Coulomb interaction it assumes a screened Debye-Hückel potential $U_{DH}(r) = \lambda_B k_B T \frac{\exp(r/r_D)}{r}$, where λ_B is the Bjerrum length given by $\lambda_B = \frac{e^2}{4\pi\epsilon_s\epsilon_r k_B T}$, with e denoting the elementary charge and ϵ_s, ϵ_r are the dielectric constants. The two competing theories both predicts $L_E \propto r_D^y$, however the exponents are $y = 1$ or $y = 2$, depending which perturbation approach one believes more. To test

the theoretical approaches, a series of molecular dynamics (MD) and Monte Carlo (MC) simulations have been presented [2] with the result, that neither theoretical approach is correct in the intermediate regime, but that the exponent y can vary continuously between 0.5 and 2. Only very recently a field theoretic renormalization group analysis was able to shed some additional light onto this problem[3].

A serious drawback of the Debye-Hückel theory is that it presupposes only weak variations in the density of the counterions, and neglects all correlation effects. One can therefor doubt if this potential is able to describe the chain conformations adequately [4]. Also counterion condensation can not properly be handled. To tackle these questions computer simulations provide the necessary tools, because here one does not need to rely on excessive simplifications. One can treat the counterions explicitly and can also utilize the full long range Coulomb potential. We try to summarize here recent results of MD simulations on *systems* of polyelectrolyte chains in solution. Details of the studies can be found in the original literature [5, 6, 7]

2 MODEL

Our model of a flexible polyelectrolyte chain consists of N_p bead-chain polymers with N_m monomers which are located in a simulation box with periodic boundary conditions (3D torus). From these monomers a fraction f is monovalently charged. The number of counterions, N_c, with valence v is then chosen such that the overall system is electrically neutral. If we have, for example, N_q charges on a polymer chain, then the number of counterions with valence v is given by $N_c = \frac{N_p N_q}{v}$, and the total number of charges in the system is $N_{tq} = 2N_c$. All *hydrophilic* monomers are given an effective size through a pure repulsive Lennard-Jones potential, representing thus a polymer chain in a good solvent:

$$U_{LJ}^r(r) = \begin{cases} 4\varepsilon_{LJ} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & : \quad r \leq r_{min} = 2^{1/6}\sigma \\ 0 & : \quad \text{otherwise} \end{cases} \tag{1}$$

All chain monomers, which model the *hydrophobic* or poor solvent case, interact via a standard Lennard-Jones potential with attractive part:

$$U_{LJ}^a(r) = \begin{cases} 4\varepsilon_{LJ} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] & : \quad r \leq r_c = 2.5\sigma \\ 0 & : \quad r \geq r_c = 2.5\sigma \end{cases} \tag{2}$$

All *chain* monomers are in addition connected by the FENE (finitely extended nonlinear elastic) bond potential,

$$U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right). \tag{3}$$

All *charged* monomers posses in addition the full Coulomb energy

$$E_c(r_{ij}) = \frac{\lambda_B k_B T v_i v_j}{r_{ij}},$$

(4)

where v_i is the valence of the ith charged monomer.

The electrostatic energy of the box is calculated with the Ewald formula

$$E_c = E^{(r)} + E^{(k)} + E^{(s)}$$

(5)

where the contribution from real space $E^{(r)}$, the contribution from reciprocal space $E^{(k)}$, and the self energy $E^{(s)}$ are given by

$$E^{(r)} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{m}\in\mathbb{Z}^3}' q_i q_j \frac{\text{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{m}L|)}{|\mathbf{r}_{ij} + \mathbf{m}L|}$$

(6)

$$E^{(k)} = \frac{1}{2}\frac{1}{L^3} \sum_{\mathbf{k}\neq 0} \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} |\tilde{\rho}(\mathbf{k})|^2$$

(7)

$$E^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$$

(8)

and the Fourier transformed charge density $\tilde{\rho}(\mathbf{k})$ is defined as $\tilde{\rho}(\mathbf{k}) = \sum_{j=1}^{N_q} q_j\, e^{-i\,\mathbf{k}\cdot\mathbf{r}_j}$.

The Ewald parameter α, which has the dimension of an inverse length, tunes the relative weight of the real space and the reciprocal space contribution, but the final result is of course independent of α. The **k**-vectors form the discrete set $\{2\pi\mathbf{n}/L : \mathbf{n} \in \mathbb{Z}^3\}$, and we use tin-foil boundary conditions, hence there is no dipole correction term. The standard Ewald method has computational effort at best of $\mathcal{O}(N_{tq}^{3/2})$, which limits the size of the samples. To overcome this limitation, we use for $E^{(k)}$ a particle mesh Ewald algorithm (PME) that uses discrete charge assignments and fast Fourier transforms (FFT), and accordingly scales for $E^{(k)}$ as $\mathcal{O}(N_{tq}(\log N_{tq})^{3/2})$ [8]. Note, however, that this is not the most effective algorithm, as was shown recently [9].

In all our performed molecular dynamics (MD) simulations we had no salt ions and no explicit solvent molecules. The solvent,however, was implicitly taken into account via a Langevin thermostat with damping constant $\Gamma = \tau^{-1}$, with time step 0.00125τ at constant temperature $k_B T = 1\epsilon$. The number of MD steps was chosen such that the typical observables like the end-to-end distance $R_E = \sqrt{\langle \vec{R}_E^2 \rangle}$ or the radius of gyration R_G had sufficiently relaxed, which happened usually after $500\,000$ up to $5\,000\,000$ MD steps.

3   STRONGLY CHARGED POLYELECTROLYTES IN GOOD SOLVENT

3.1 MONOVALENT COUNTERIONS

The first investigation of totally flexible many chain polyelectrolyte systems in good solvent with explicit monovalent counterions was performed already some years ago [5]. The simulations were done mostly with systems of 8 or 16 chains with $N_m = 16$, 32, and 64. Instead of the PME algorithm a spherical approximation in a truncated octahedral simulation box was used, which is for smaller values than $N_{tq} \approx 500$ faster than the PME method. More details of the whole study can be found in [5].

In this work it was demonstrated that the simple bead-spring model can actually be compared to real polyelectrolytes, because the experimental values for the osmotic pressure and the maximum position in the interchain structure factor are successfully being reproduced. One of the important findings was that the rodlike chain is found to be a rarity already in the dilute limit. Counterion condensation can dramatically shrink the polyelectrolyte chain. The end-to-end distance shortens significantly as the density increases from the dilute saturation value to the overlap value. The chain structure is highly asymmetric at the very dilute saturation density and the scaling with respect to N_m is asymmetric, but as the overlap density is approached, the structure is less asymmetric and the scaling becomes approximately symmetric. On long length scales the chain structure continuously changes from very elongated to neutrallike coils. Yet, on short length scales, the chain structure is density independent and elongated more than neutral chains. The findings for the single Bjerrum length $\lambda_B = 0.883\sigma$ are summarized in Fig. 1. It was found that in the dilute limit the scaling for the extension perpendicular to the chain was $R_\perp \propto N^{0.65-0.70}$, and for the extension parallel it was $R_\parallel \propto N^{0.90-1.00}$. Near the density, where the rodlike chains in disordered solution would overlap, $\rho \sim N^{-2}$, $R_\perp$ starts to grow on the expense of $R_\parallel$ until at the overlap density ρ^* the effective exponent is about 0.82. This transition regime ranges from $\rho \sim N^{-2}$ to about $\rho \sim N^{-1.4}$ where the coils start to overlap and one eventually reaches $\nu = 1/2$ in the semidilute regime. The exponents reported should not necessarily be taken as asymptotic $(N \rightarrow \infty)$, however they should be relevant for many experimentally systems.

In a recent study [6] a large MD simulation of 200 chains with $N_m = 32$ was performed to determine if with these large systems $(N_{tq} = 12\,800)$ any large scale ordering phenomena could be observed. The idea of the onset of ordering is one of the possible explanations for the Fuoss-Strauss effect in the reduced viscosity η_r, which shows a dramatic increase and subsequently a decrease of η_r, as the polymer concentration is decreased. The pure MD simulation showed so far no sign of correlations or ordering, however it was found that the center of mass diffusion of the monomers was just too slow to move the monomers far enough. It needs definitely accelerated algorithms (MC or MD) to settle this question in a large scale computer simulation, which will be pursued in the future.
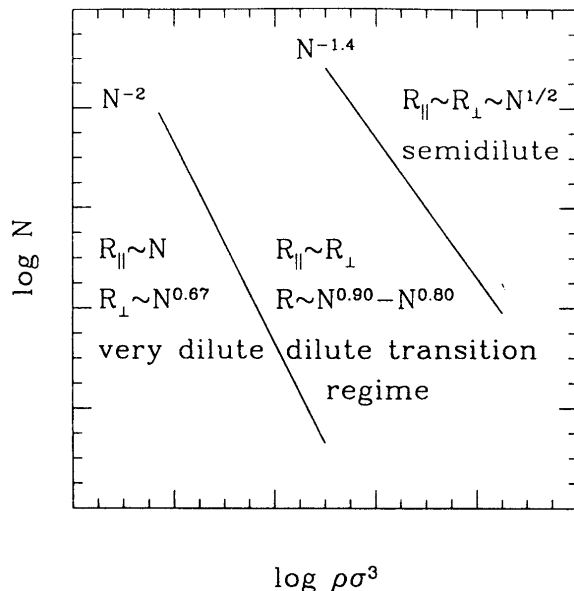
Figure 1: A structure diagram for $\lambda_B = 0.833\sigma$, which shows the dilute limit, the contraction below the overlap density ρ^*, and the completely screened limit at large ρ.

3.2 MULTIVALENT COUNTERIONS

In this set of first simulations we usually considered eight chains in the central box with a chain length of $N_m = 106$ and a charge fraction of $f = 1/3$. We varied the valence of the counterions from one to three, and chose always $\lambda_B = 3\sigma$, thus the monovalent systems were just below the critical Manning threshold. The weighted density of charged particles, $\rho_c = \sum_i^{N_{tq}} \frac{v_i}{L^3}$ was varied from $10^{-1}\sigma^{-3} \ldots 10^{-6}\sigma^{-3}$. The starting configurations were set up as rod configurations with randomly distributed counterions, or as a random walk, if the rods would not fit in the central box. That both initial configurations lead to the same equilibrium value for R_E can be seen in Fig. 2. Another point to note is, that both time series converge very rapidly, even before they are fully equilibrated. This is due to the fact, that the Coulombic repulsion of the chain monomers provide a very fast initial rearrangement of the chain, but that the equilibrium conformation is only reached, after the counterion cloud has itself arranged around the polymers. If one looks on the end-to-end distance R_E as a function of density for the different valences, see left side of Fig. 3, one notices that for high polymer concentrations all three valences have basically the same R_E, they show SAW behavior. For the semi-dilute range the monovalent systems elongate very fast, whereas the divalent systems elongate much slower, and the trivalent system actually *contracts*. This is due to the fact that a trivalent counterion can bind more than one charged chain monomer, so that the chain can "wrap around" the counterion,
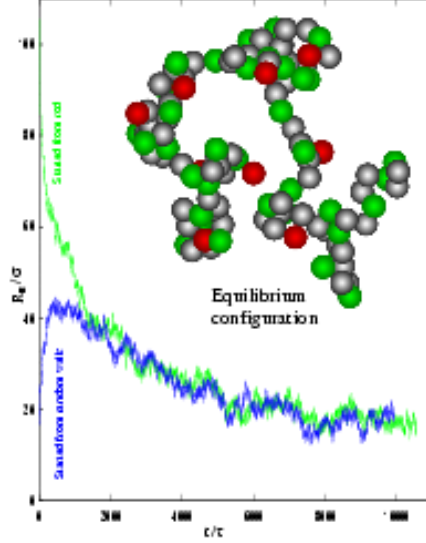
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Figure 2: Time series of the end-to-end distance R_E versus simulation time t/τ, plus a typical equilibrium configuration for a trivalent system at $\rho = 10^{-5}\sigma^{-3}$.

or the counterion can even bridge two far apart regions of the chain, as can be seen in the configuration in the upper part of Fig. 2. For lower density the trivalent chains elongate much slower, so that they will reach a rod like configuration at much lower concentrations. Even at this dilution the chains still show much structure due to the discrete counterions.

Another interesting quantity to look at is the fraction of counterions found up to a distance r, which we denote by the *integrated* ion distribution function $P(r)$, shown on the right side of Fig. 3. Especially for low concentrations, this function gives a good estimate to determine the fraction of *condensed* counterions, because one can clearly see a plateau value for $P(r)$, meaning that the ions can be separated in bulk counterions far apart from the polymer, and a distinct layer of condensed counterions. For higher concentrations and lower valences, however, this distinctions gets less pronounced. One observes that the condensed fraction of counterions, which we denote by C, depends strongly on the density and valence. With increasing density and valence the condensed fraction increases, and assumes for the highest investigated density $\rho = 10^{-1}\sigma^{-3}$ the value $C = 1$ for all three valences. The Manning predictions for these systems are $C = 0(v = 1)$, because for the monovalent systems we are slightly below the critical Manning parameter, and $C \approx 1/2(v = 2)$ and $C \approx 1/3(v = 3)$ for the other valences.

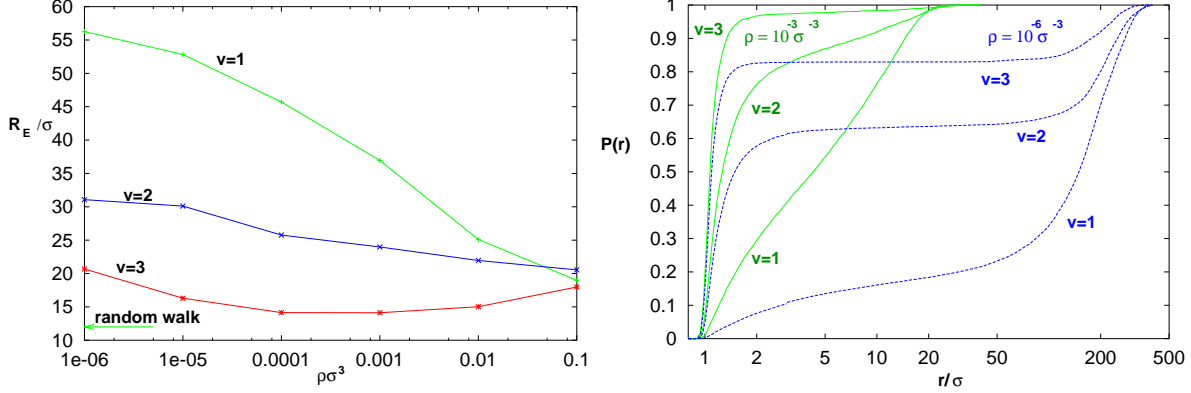A third interesting aspect to look at is the counterion exchange dynamics. If one

Figure 3: Left: R_E vs. ρ for valences $v = 1...3$; right: integrated ion distribution function P(r) vs. distance r for $\rho = 10^{-3}\sigma^{-3}$ and $\rho = 10^{-6}\sigma^{-3}$, each for valences $v = 1...3$.

defines the set of condensed ions as $\mathbb{K}_d^j(t)$, which contains all ions being within distance d on polymer j at time t, then one can define a conditional condensation fraction $c_d((t|t_0)$ as follows:

$$c_d\left(t|t_0\right) := \left\langle \frac{|\mathbb{K}_d^j(t) \cap \mathbb{K}_d^j(t_0)|}{|\mathbb{K}_d^j(t_0)|} \right\rangle_j \tag{9}$$

This equation simply means, count the number of ions which are on time t as well as on time t_0 condensed on polymer j, normalize by the number of condensed ions on polymer j at time t_0, and average then over all polymer chains j. The normalization is such, that $c_d(t_0|t_0) = 1$. Fitting this quantity to an exponential Ansatz $c_d(t|t_0) \sim A + B \exp{-t/t_{\text{relax}}}$ gives information about the exchange dynamics of the counterions. We find that with increasing valence at constant density the mobility decreases, and that the mobility also decreases with decreasing density at constant valence. The value of t_{relax} is of the order of $10\,000\tau$, showing the very slow dynamics at low densities.

4   POLYELECTROLYTES IN POOR SOLVENTS

The investigations so far dealt only with polyelectrolytes in good solvent, to facilitate the comparison to known systems such as neutral polymer systems. Most experimentally investigated polyelectrolytes, however, posses a hydrophobic backbone. This results in a competition between the solvent quality, the Coulombic repulsion, and the entropic degrees of freedom, which can lead to totally different behavior[6]. The simulations presented below used 16 chains of length $N_m = 94$, with a charge fraction of $f = 1/3$, and monovalent counterions. The hydrophobic interaction strength was tuned by means of

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the Lennard-Jones parameter ε_{LJ} of Eq. (2) that was chosen such that the finite chain shows an effective random walk behavior ($\varepsilon_{LJ} = 1.5$) for the density $\rho = 10^{-4}\sigma^{-3}$.

The polymer density ρ can be used as a very simple parameter to separate different conformation regimes. This can already be seen in the plots of the end-to-end distance R_e and $r = \frac{R_E^2}{R_G^2}$ versus ρ in Fig. 4. At very high densities the electrostatic interaction is highly screened, so that the hydrophobic interaction wins, and the chains collapse to dense globules. If one slightly decreases the density, the chains can even contract further, because there are no more steric hinderences from the other chains or counterions, and the screening is smaller. The collapsed globules, however, have still a net charge, and repel each other, so that this phase resembles a charged stabilized colloid or microgel phase. With decreasing density the electrostatic interaction will dominate over the hydrophobic one. The chains will tend to elongate, assuming pearl-necklace conformations, see Fig. 5, as they have been predicted for weakly charged polyelectrolytes in Ref. [10]. The more the chain stretches, the smaller become the locally compact regions. Reducing the density even further then leads to a strongly elongated blob pole, which is however, due to the intra chain entropy and the hydrophobicity, still far from an ideal stiff cylinder, and shows local structure.
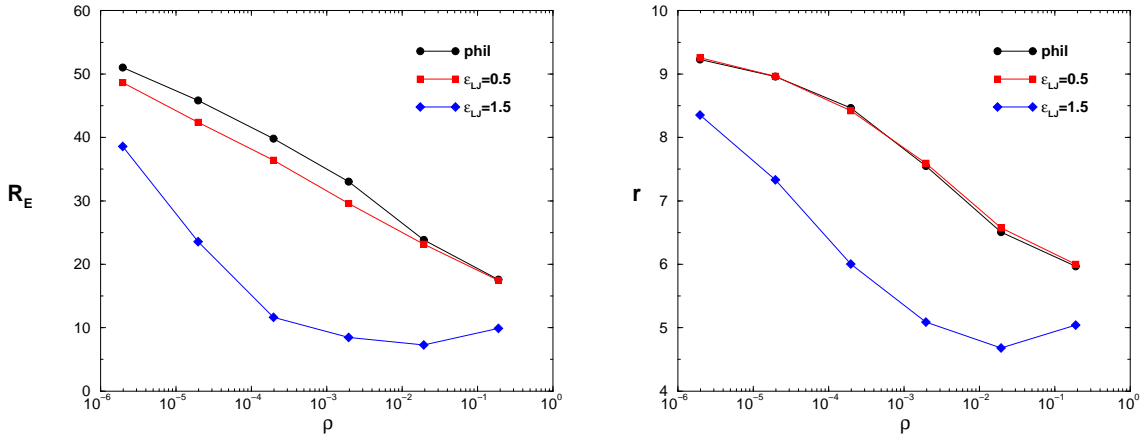

Figure 4: R_E (left) and r (right) versus density ρ for hydrophilic (phil), weak hydrophobic ($\epsilon_{LJ} = 0.5$), and strongly hydrophobic ($\epsilon_{LJ} = 1.5$) chains

5   CONCLUSION

We summarized the recent efforts which were pursued to learn more about linear flexible polyelectrolytes in solution. The investigated systems are already large enough to repro-
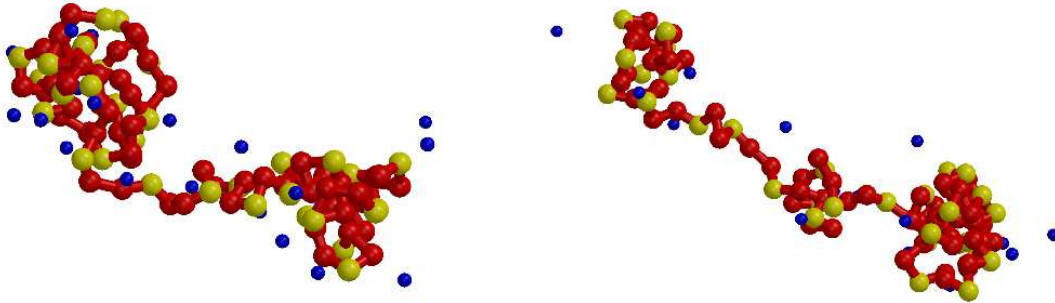
Figure 5: Typical polyelectrolyte conformation for the densities $\rho = 2 \cdot 10^{-4} \sigma^{-3}$ (left) and $\rho = 2 \cdot 10^{-5} \sigma^{-3}$ (right). Only counterions within 10 σ of the chain are considered.

duce experimental measurements such as the osmotic pressure or the intrachain structure factor. The incorporation of multivalent counter ions alters the chain structure drastically. Such aspects can clearly never be captured by a Debye-Hückel approach. The integrated ion distribution function P(r) seems to be a good measure of how one can separate the condensed layer of counterions from the bulk counterions, and shows clearly that the fraction of condensed ions is density dependent.

With the beginning investigations of polyelectrolytes in poor solvents one can also compare the simulations more easily to experiments. An interesting aspect of hydrophobicity is, that already weak hydrophobicity can alter the chain structure, and that with strong hydrophobicity the system can produce a physical gel. The behavior of R_E versus the density looks very similar to the behavior which is found for hydrophilic systems with trivalent counterions.

Still many things remain to be done. To name just a few, the whole range of semiflexible linear chains is still to be investigated. A detailed study of Manning condensation is also lacking. To analyze properly any sort of aggregation phenomena, one needs to simulate much larger systems. This can, up to now, only be pursued, if one has an efficiently parallized code, which incorporates a mesh Ewald method or any other algorithm whose CPU-time scales linearly with the total number of charges N_{tq}.

6 ACKNOWLEDGMENTS

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